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**THEORETICAL STUDIES OF ENERGETIC MATERIALS**

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### **Abstract**

The research supported by AFOSR-AASERT grant F49620-95-L-0411 (parent grant F49620-95-L-0310) for the period 1 June 1995 to 31 May 1999 is described. The purpose of the research is the formulation of methods and realistic models for studying the fundamental properties and behavior of insensitive energetic materials. The work performed during this grant focused on the development of intramolecular potentials to describe the vibrational dynamics of the "insensitive" energetic materials NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one) and ANTA (5-amino-3-nitro-1H-1,2,4-triazole). In addition, the applicability of intramolecular dynamics diffusion theory (IDDT) for computing reaction rates in large, complex systems such as energetic molecules and solids was demonstrated.

## I. Introduction

The research performed during the grant period contributed to the long-term objectives of this research program, which are to develop theoretical methods and perform calculations to investigate fundamental, elementary processes (ultimately including chemical reactions) in high energy high density materials (HEDM). The work supported by this grant focused on the development of intramolecular potentials to describe the vibrational dynamics of "insensitive" energetic materials, namely, NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one) and ANTA (5-amino-3-nitro-1H-1,2,4-triazole). In addition, we also carried out a study to extend the applicability of intramolecular dynamics diffusion theory (IDDT) to treat complex chemical reactions. The IDDT provides a practical means of computing reaction rates in large, complex systems such as energetic molecules and solids.

## II. Research

The initial stage of the research program to develop realistic models for simulating physical and chemical processes in solid energetic materials has involved the development of accurate potentials to describe the vibrations of the molecules of interest. These will eventually be incorporated into the crystal models that are being developed as a part of the work supported by the parent grant. The potentials for the molecules were formulated by carrying out *ab initio* calculations for equilibrium geometries to determine the fundamental frequencies and geometries. These results were then scaled to experimental frequencies to construct force field potentials. Accurate force field potentials were developed for NTO and ANTA. Abstracts of the two publications resulting from this work follow:

D. C. Sorescu, T. R. L. Sutton, D. L. Thompson, D. Beardall, and C. A. Wight, *Theoretical and Experimental Studies of the Structure and Vibrational Spectra of NTO*, J. Mol. Struct. **384**, 87-99 (1996). Abstract: The structure and vibrational spectra of the high explosive 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO) have been determined by *ab initio* molecular orbital calculations at the Hartree-Fock and second-order Møller-Plesset levels and by density functional theory (B3LYP). Experimental frequencies for the molecule have been determined from infrared spectra of pure NTO films and NTO

molecules isolated in an argon matrix at 21 K. A force field for gas phase NTO has been obtained based on calculated results at the MP2/6-311G\*\* level. In addition, a force field for solid state NTO has been constructed using the experimental vibrational frequencies for NTO films and scaled *ab initio* vibrational frequencies. Differences between the solid state and gas phase results indicate that the environment and preparation procedure exert a marked influence on the spectral characteristics of the NTO molecule.

D. C. Sorescu, C. M. Bennett, and D. L. Thompson, *Theoretical Studies of the Structure, Tautomerism, and Vibrational Spectra of 3-Amino-5-nitro-1,2,4-triazole*, J. Phys. Chem. A **102**, 10348-10357 (1998). Abstract: The structure, tautomerism and vibrational spectra of the highly explosive 3-amino-5-nitro-1,2,4-triazole (ANTA) molecule were studied by *ab initio* molecular orbital calculations at the Hartree-Fock (HF), second-order (MP2) and fourth-order (MP4) Möller-Plesset levels and by density functional theory (DFT) both in gas phase and in solution. It was found that in the gas phase the most stable tautomer is 2H-ANTA (3-amino-5-nitro-1,2,4-2H-triazole) at the HF level, while at MP2, MP4 and DFT levels the most stable tautomer is 1H-ANTA (3-amino-5-nitro-1,2,4-1H-triazole). For the 2H-ANTA tautomer, the calculated MP2 and DFT structures agree well with the experimental X-ray structures, but with the twisting of the nitro and amino groups much larger than in the solid state. The predicted IR spectra are given for all tautomers. The calculated fundamental vibrational frequencies at the DFT level generally compare well with the MP2 results. In the case of 2H-ANTA, the C-NO<sub>2</sub>, C-NH<sub>2</sub> and N-H bond dissociation energies were estimated to be 67.1, 112.9 and 96.3 kcal/mol, respectively. Based on the structural and spectroscopic results calculated at the MP2 level, a classical force field for gas phase 2H-ANTA was developed. The effects of environment polarity on the conformations and energetics of 1H-ANTA and 2H-ANTA tautomers were studied by performing calculations at the DFT level within the Onsager continuum solvation model. The results obtained for the dielectric constants  $\epsilon = 4.8, 18.5$ , and  $78.4$  suggest that in a polar solvent the most stable tautomer is 2H-ANTA, in agreement with the experimental studies.

In addition to the formulation of accurate vibrational potentials, we further developed diffusion theory methods for treating complex chemical reactions. The abstract of the resulting publication follows:

Y. Guo, D. V. Shalashilin, J. A. Krouse, and D. L. Thompson, *Intramolecular Dynamics Diffusion Theory Approach to Complex Unimolecular Reactions*, J. Chem. Phys. **110**, 5521-5525 (1999). Abstract: A further development of the intramolecular dynamics diffusion theory (IDDT) [J. Chem. Phys. **107**, 6204 (1997)] for computing unimolecular reaction rate constants in the IVR-controlled regime is described. The approach is based on Kramers' energy diffusion theory, with the reaction coordinate taken as the subsystem and the rest of the vibrational modes as the bath. The method provides a practical means of obtaining the rate constants in the IVR-controlled regime at considerable savings of computer time compared to the usual classical trajectory simulations. Its accuracy has been demonstrated in our earlier applications to some simple bond-fission reactions. In

the study described here the idea of intrinsic reaction coordinate (IRC) is used to extend the IDDT approach to more complicated systems for which simple reaction coordinates are not easily identifiable. The basic idea is to take the IRC as the subsystem and the transverse vibrational modes as the bath. The method is applied to the unimolecular dissociation of REX (hexahydro-1,3,5-trinitro-1,3,5-triazine), and the rate constants calculated using IDDT are in good agreement with classical trajectory simulations over a wide range of energies, suggesting that the approach may be generally applicable to large polyatomic systems.

### III. Publications

D. C. Sorescu, T. R. L. Sutton, D. L. Thompson, D. Beardall, and C. A. Wight, *Theoretical and Experimental Studies of the Structure and Vibrational Spectra of NTO*, J. Mol. Struct. **384**, 87-99 (1996).

D. C. Sorescu, C. M. Bennett, and D. L. Thompson, *Theoretical Studies of the Structure, Tautomerism, and Vibrational Spectra of 3-Amino-5-nitro-1,2,4-triazole*, J. Phys. Chem. A **102**, 10348-10357 (1998).

Y. Guo, D. V. Shalashilin, J. A. Krouse, and D. L. Thompson, *Intramolecular Dynamics Diffusion Theory Approach to Complex Unimolecular Reactions*, J. Chem. Phys. **110**, 5521-5525 (1999).

### IV. Grant Personnel

The following graduate students were supported during the course of this grant:

Ms. Teresa R. L. Sutton

Mr. Carl M. Bennett

Mr. Justin A. Krouse